Practical Challenges in the Development of Photoelectrochemical Solar Fuels Production

Mark Spitler,[1†] Miguel Modestino, [2] Todd Deutsch,[3] Chengxiang Xiang,[4] James Durrant,[5] Daniel Esposito,[6] Sophia Haussener,[7] Stephen Maldonado,[8] Ian D. Sharp,[9] Bruce Parkinson,[10] David Ginley,[11] Frances Houle,[12] Thomas Hannappel,[13] Nathan Neale,[14] Daniel Nocera[15] and Paul McIntyre[16]

This article addresses the challenges presented by photoelectrochemical solar fuels technology in a discussion that begins with a functioning device and proceeds to the more fundamental science of its component parts. In this flow of discussion issues are addressed that frame the discussion for the next, increasingly more fundamental topic. The analysis begins with a discussion of the need for an analytical facility necessary for confirmation of reported efficiencies of solar fuels device prototypes and then progressively narrows its scope to prototype design, the discovery of novel materials and the design of durable interfacial structures for fuels evolution. Molecular hydrogen will be considered first as the target fuel since many of the challenges with hydrogen production are general and applicable to the more complex CO_2 reduction, which will be treated as a supplementary subject.

1. Department of Chemistry, University of North Carolina, Chapel Hill, NC, USA
2. Department of Chemical and Biomolecular Engineering, New York University, New York, NY, USA
3. National Renewable Energy Laboratory, Chemistry and Nanoscience Center, Golden, CO, USA
4. Joint Center for Artificial Photosynthesis, California Institute of Technology, Pasadena, CA, USA
5. Department of Chemistry and Centre for Plastic Electronics, Imperial College London, London and SPECIFIC IKC, University of Swansea, U.K.
6. Department of Chemical Engineering, Columbia University, New York, NY, USA
7. Institute of Mechanical Engineering, EPFL, Lausanne, Switzerland
8. Department of Chemistry, University of Michigan, Ann Arbor, MI, USA
9. Walter Schottky Institute, Technical University of Munich, Munich, Germany
10. Department of Chemistry, University of Wyoming, Laramie, WY, USA
11. National Renewable Energy Laboratory, Golden, CO, USA
12. Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, CA, USA
13. Institute for Physics, University of Ilmenau, Ilmenau, Germany
14. National Renewable Energy Laboratory, Golden, CO, USA
15. Department of Chemistry, Harvard University, Cambridge, MA, USA
16. Department of Materials Science and Engineering, Stanford University, Stanford, CA, USA

† The corresponding author is a Visiting Scholar at the University of North Carolina. E-mail: spi1tlerm@email.unc.edu

All authors contributed equally to this work, with the sequence of the authors reflecting the order of their contribution in the text.

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Introduction

Research over the past decades in the field of photoelectrochemical (PEC) solar fuels production has been a long-term effort that has sought a pathway to the production of a practical chemical fuel through the absorption of solar photons at a semiconductor electrolyte interface, whether it be molecular hydrogen or an energy-rich carbon-based compound that is evolved,.[1-3] The seminal work in this field was published in 1972 by Fujishima and Honda. Compared with the significant advances in solid state photovoltaic (PV) devices since that year, progress in PEC solar fuels technology has been slow and beset with challenges in scientific discovery, materials and design.

Many overviews and reviews on PEC solar fuels have been published over the past decades and reveal a worldwide interest in this field that has provoked calls for a more coordinated, international effort.[4] Examination of these reviews show them to cover detailed technical analyses, prototype design considerations and cost estimates for device production.[5-10] This work, however, takes a different approach to the topic in connecting the selection of a business market for PEC solar fuels production subsequently to prototype design, the scale of the active area of the device, and the scope of research on reactive interfaces central to such a device. It addresses the obstacles to the development of PEC technology in a flow of discussion that begins with a functioning device and then proceeds to the more fundamental science of its component parts. At each step issues will be discussed that facilitate the next, increasingly more fundamental topic, a process that illustrates how the scope of research can be narrowed successively to its most relevant elements. The discussion will focus on molecular hydrogen as a simple example of a solar fuel with the more difficult problem of CO2 reduction being treated as a secondary topic.

 The first of four topics for discussion concerns an analytical facility, one that is needed for confirmation of reported efficiencies of solar fuels device prototypes. In the examination of an analytical facility for confirmation of efficiencies, it is noted that central facilities exist for confirmation of photovoltaic (PV) solar cell efficiencies, with bi-annual publications of the highest certified efficiencies,[11] but not for PEC solar fuels evolution. The question is posed as to what additional considerations would be necessary to create a facility devoted to the measurement of the efficiency of solar fuels production. Within this discussion a recognition is made that standard prototype designs may be needed for this testing. The follow up topic concerns the challenges inherent in the design and construction of system prototypes for PEC fuels production. The appropriate size and configuration must be determined for a prototype or device given the size limitations of the measurement capabilities analytical facilities. These constraints on the prototype impose an electrode size and the appropriate concomitant electrochemical engineering design. The photoactive dimensions identified in these discussions provide an area to which the semiconductor light absorbers and catalytic surfaces must be scaled up. This introduces the next challenge where the large area deposition of these solids may be on the order of dm^2. Known semiconductors may possibly be coated at this dimension, given that they possess the requisite stability and photoefficiency, but it is likely that novel semiconductors will be needed and combinatorial and computational approaches to their discovery are addressed. Given the areas for photoactive surfaces and the electrochemical engineering in the prototype design, the last topic on the durability of the photocatalytic surface for fuels production from sunlight will be examined, whether the surface be the bare semiconductor or deposited metallic or molecular catalysts. With the assumption that no catalytic interface is infinitely stable, this discussion concerns interfacial electrode structures from the semiconductor bulk to solution, the pathways for controlled chemical kinetics, and the system to be scaled up, all to yield a desired turnover number that is cost-effective for the device as a whole.

In contrast to the early-stage character of PEC solar fuels technology, the development and marketing of PV devices for electricity production has passed through a many-decade period to become a practical and reliable, if intermittent, source of power throughout the world. It is therefore useful to analyze the historical progress of PV devices as a reference point in this discussion of PEC solar fuels technology. The progress of the solid-state photovoltaic device since 1976 can be depicted through the learning curve given in Fig.1a where the market price of electricity produced by a PV module is plotted against the installed base of PV modules around the world[12] and is seen to describe a declining curve where the market for the PV modules grows as the price of the module drops. In the beginning these markets may have been contract work for specialty applications such as satellite power sources or power in remote locations, but they have grown in size to represent the technology's transformation into a commodity producer of electricity for the general population. It is possible to grow a market in this way with a continual drop in cost of the product if the market is elastic and responds in demand to compensate in proportion for the loss of the per piece revenue, a situation which is guaranteed by the massive power consumption of modern economies. However, the deviations in Fig. 1a of the learning curve data from the average line for the price drop shows that the supply-demand elasticity is not always immediate in response. The manufacture of the PV device did not suddenly begin at the massive scale and low cost of today, but approached it with the technological and marketplace constraints of the

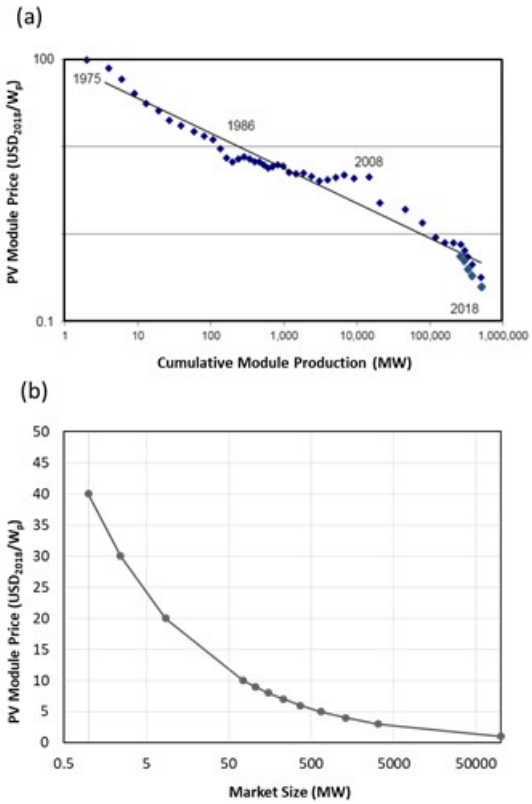

Figure 1 (a) A learning curve plot using data shows the history of the PV module peak cost ($/W) with respect to the magnitude of the installed base at that cost. (Modified from ref. 12) (b) Using the fitted line of Fig. 1a, the change of the installed base of PV from one year to the next can be plotted as a function of PV module cost for that year in order to show the size of the market for each cost point.

day. For example, if the change in cumulative production in each successive year is plotted as a function of the module price for that year, the curve in Fig. 1b is obtained. The implication of Fig. 1b, which can be interpreted to represent the relation between PV market and PV price, is that there was a market for PV devices for all costs ranging from $50-$100/W down to the spot price level in Fig. 1a of $.50/W. Small producers of PV modules made a business at the small scale and at high cost, but it is not until the market appetite became very large and economies of scale could be realized that large corporations became interested in the production of this device.

It should be expected that a similar learning curve would be encountered for fuel producing PEC technology. The price of PEC fuels in the initial products in the field will not immediately match that of currently available fossil fuels, but the question to be posed is if there is a business to be made for PEC solar fuels at that initial and high price point as was historically possible for PV at the costs higher than $1/W. One starting point for the discussion on PEC solar fuels is that it must be cost competitive with a PV device connected to a commercial electrolyzer. Cost estimates of this capital-intensive combination have been made[13] for plants producing 10,000 kg of H_2 per day, which is certainly far down the learning curve of Fig. Ib. However, the costing of smaller scale PV/electrolyzer combinations need to be made to set a minimum market size for such a technology and to provide a comparison point for PEC technology.

The conversion efficiency is an important figure of merit for PEC fuel production concepts and there are many reports of efficiencies for

devices in the research literature over the past twenty years, predominately on the splitting of water with light to produce hydrogen and oxygen.[14-15] These publications remain isolated reports, however, since there exists no facility or means to obtain verification of efficiencies and performance on these various device forms. This reveals an important aspect of Fig. 1a: embedded in it are confirmed efficiency figures for PV devices provided by accredited third party analytical labs for devices assembled by commercial and academic research laboratories.

1.

An Analytical Facility for the Third Party Verifications of PEC Performance

A synopsis is provided here of the characteristics required of an analytical facility for the third party verification of PEC performance. An expanded discussion of this topic and the constraints that the facility puts upon the prototype is provided in Supplementary Information **S1**.

Building optimized prototypes is an integral part of device R&D and it is challenging, requiring significant amounts of work in the derivation of device design guidelines from modeling, the identification and fabrication of all the components, and the optimization of their operation. However, it is the analysis of prototype performance, involving all relevant metrics, that provides the necessary guidance in the scale-up strategy for promising devices. This testing provides insights into performance and stability bottlenecks at the component level only to the party that submits the device for examination and these parties will use this information to inform their R&D activities; ultimately they will reveal the efficacy of performance metrics of their devices only if it is in their interest. Academic or government researchers may opt to publish this information, but few industrial concerns will do this voluntarily.

The verification of PV efficiencies by independent laboratories has played an essential role in business decisions in the PV industry and would be expected to be a prominent and essential feature in the development of PEC products. It is also expected that the measurement practices and capabilities of the PV evaluation facilities should serve as a good model for the development of such a PEC verification capability.

Similar to PV, a PEC solar fuels evaluation facility will have to test the performance of the device under simulated solar illumination, but even this task is multifaceted. A test facility may expose the device with an artificial light source that approximates solar luminance at mid-day. It may also strive to approximate realistic conditions, where the spectral features of the sun vary in intensity and spectral character throughout the diurnal nature of a solar day. Each activity is different and each requires a different set of instrumentation. It is also evident from PV practice that the instrumental and analytical scope of a facility must also include a materials evaluation of all components of the device while under exposure to light, including the chassis and the fluid connections for fuel harvesting. A broad range of instrumental techniques and approaches will be involved in this effort and limitations in resources will restrict these capabilities, a constraint that will define the character of the analytical facility. In any case, the design of a PEC module for solar fuels production is far more complex than PV cells and this complexity will necessitate a facility for evaluation and analysis that is greater in scope and dimension than its PV counterpart.

The needs in the evaluation of the various PEC prototype formats and the capability of an analytical facility will feed into each other. There are many device architectures that the research community has developed and this variety will impose demands and constraints on a facility. The facility may need to define the format of a prototype to be tested, and in doing so, it is important to distinguish prototype devices from components of the device and to identify the needs of the customers the facility serves. Presently, a larger fraction of the research activity in the solar-fuels community is based on component development rather than device construction and analysis where the testing of component-level performance metrics guide device development at a later stage. It may be that a standard chassis for a PEC cell will have to be developed by the facility so that it can readily evaluate unique device components within the facility's physical testing constraints. It is evident that the measurement capabilities of a PEC analytical facility will possess general capabilities that encompass and exceed that of the present PV facilities. Studies and surveys have been made of the analytical techniques found by the PEC solar fuels community to be necessary for progress.[16-21] In grouping these needs as either component analysis or device performance analysis, it is evident that the former are more mature in their development since there is no third-party dedicated facility for the latter. With the present PV analytical facilities serving as an example, the measurement capability of a PEC facility will include the most significant of both. These are listed in more detail in **S1**. As with PV prototype evaluations, there are characteristics of a prototype that can artificially and incorrectly influence results, both positively and negatively.[22-24] Some are known from the work of the PV analytical facilities, but most for this relatively new technology will have to be learned by experience.

2.

Challenges in System Prototyping

An overview is given here of issues in PEC system prototyping, which is discussed in greater detail to be found in **S2**. Although many possible variations in device design are discussed, an enumeration of device designs is avoided, the goal here being to illustrate the relation between market viability, the ensuing prototype size and device design. As mentioned there are many more variables available for the design of a PEC prototype and device than there are in a PV cell. These differences result in a variety of constructs and configurations for PEC cell design that do not exist in PV technology, some that make the development of PEC technology more difficult and some that ease it. This is apparent through a comparison of a PEC solar fuels system with a commercial PV system used to drive a commercial electrolyzer. The PEC device contains the complexity of a (photo)electrolyzer and a fuel harvesting system, but minimizes the balance of systems (BOS) costs of the electricity producing PV module through incorporation of the semiconductor interface within the device.

For any design, a first goal in PEC system prototyping is to determine the appropriate size of the research prototype that will provide a guide to the potential operational performance of the scaled up dimension of a final device and a justification for continuation of development work geared towards assembly of a final prototype for manufacturing. Not all aspects of the components of the multi-faceted PEC fuels device will scale up with size with equal ease and this is learning that must be acquired. The ideal research prototype is most cost effective if its size falls within the dimension able to be handled by the analytical facility and has the lowest photoactive area that serves as an accurate measure of fuel harvesting in the device. The ca. 100 cm^2 dimension of individual PV solar cells in today's commercial market may provide a reference point in cell area at the high end.

A discussion of PEC system prototyping begins with consideration of the various design classes of possible PEC devices. From a technical perspective, PEC fuel production may be classified into two groups, one being photoelectrochemical and the other being photocatalytic in function, where low cost examples can be found for both.[5,25,26] Photoelectrochemical designs will expose a planar surface to light and may have catalytic surface

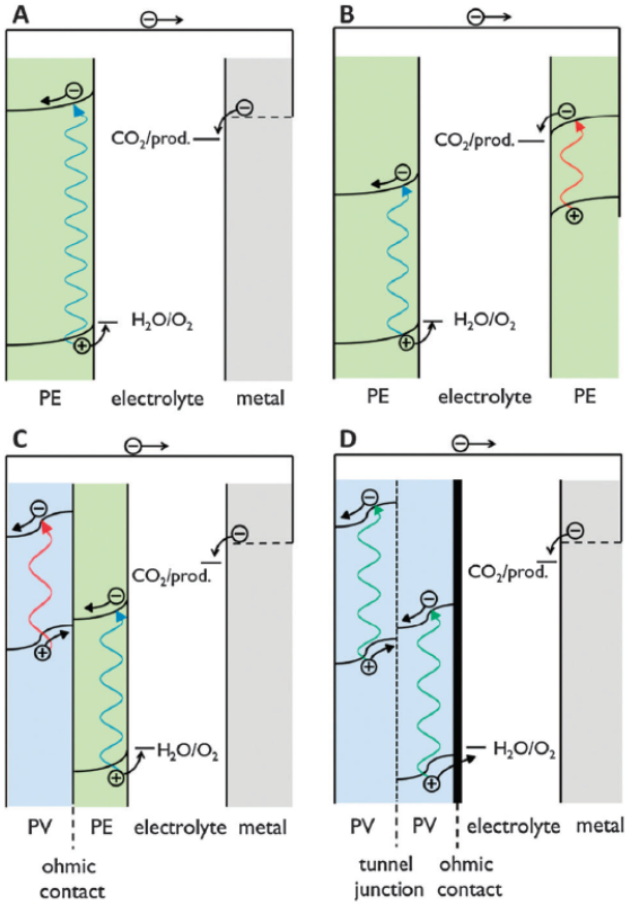

Fig. 2 Four configurations are given for PEC devices for solar fuels evolution. Single and tandem designs with one or two reactive photoactive absorbers are shown as well as corresponding designs featuring buried PV junctions. (With permission from ref. 30. Copyright 2014 Royal Society of Chemistry)

species for water splitting and buried junctions to drive the photocurrent. A prime example of photocatalytic systems is where suspensions of low cost, light absorbing particles can effect water splitting.[27-29]

In these groups one can utilize a single absorbing material to drive PEC fuel production or one can employ a tandem design, where the fuel production is driven by absorption of two photons by two different solids, as is shown in Fig. 2.[30] The two absorbing semiconductors can also be assembled as a buried solid state junction with various forms of contacts between them, ohmic and tunnel junction being examples depicted in Fig. 2C and Fig. 2D. The two approaches of single or double absorber have inherent performance differences, with the tandem approach offering higher theoretical efficiencies.[31] For catalytic suspensions a dual bed arrangement, each with a separate absorber, makes use of the two photon approach to drive the reaction and allows for the possibility of product separation in different places, as would be preferable for hydrogen and oxygen. From an engineering perspective the single photon approach is preferable, but higher efficiencies may warrant the efforts to develop the more complex two photon design. For many of these configurations, a membrane will play a key role in conducting currents and isolating products, although there are examples where it is avoided.[32]

PEC system prototyping must also include a framework for assembly of the components of the system design and the interrelationships of these components. Industrial R&D personnel and engineers can survey the range of variables to consider in the design of a PEC prototype in terms of their firm's technical and manufacturing capabilities and can look backward from the market and product towards research to define inventions to be made and research to be done. However, from the viewpoint of one in basic research, the task of designing a prototype system that might one day be scaled up and implemented in a practical application can be overwhelming. If a researcher has discovered a promising new photoabsorber, for example, and wishes to incorporate this material in a PEC device, it is very challenging to select the most appropriate electrolyte, co-catalysts, coatings, if needed, let alone to decide from the many available device/chassis options, ancillary components, and product collection and separation mechanisms. There can be 10^2-10^4 different combinations of materials and device design options.[10,33]

Referred to as decision trees, these frameworks for the selection of the most logical combinations of these PEC system variables can be decided based on pre-defined constraints for a given researcher or business. It is a hierarchical or tiered decision support tool that presents options for the design of a PEC device in a sequential manner based on starting assumptions, constraints, parameter sensitivities, and the primary performance figure of merit, such as efficiency or cost. An example is given in Fig. 3 where the starting point is a new absorber material and decisions are made at decision points D1 through D5 to design a prototype system. A detailed explication of this particular decision process is given in **S2**. There is not a single ideal decision tree that can or should be applied to all situations. A key parameter in such a decision process is the selection of the electrolyte, which includes aqueous alkaline, aqueous acid and aqueous salt solutions, solid electrolytes, and mixed aqueous/nonaqueous electrolytes, some of which are known from the electrolyzer and fuel cell research.

Any commercial enterprise with an interest in the demonstration of large, square meter sized devices, where experience is limited at this time,[6,34,35] would have to create the appropriate decision framework and design guidelines. The firm might lean upon synergies to be found in the scaling approaches used in related technologies such as high and low-temperature fuel cells and electrolyzers, photovoltaics, microfluidic systems, or electrochemical industrial processes. However, there are caveats in this approach. PEC devices are inherently multi-physical and usually include more complex physics and chemistry than many of the other technologies,

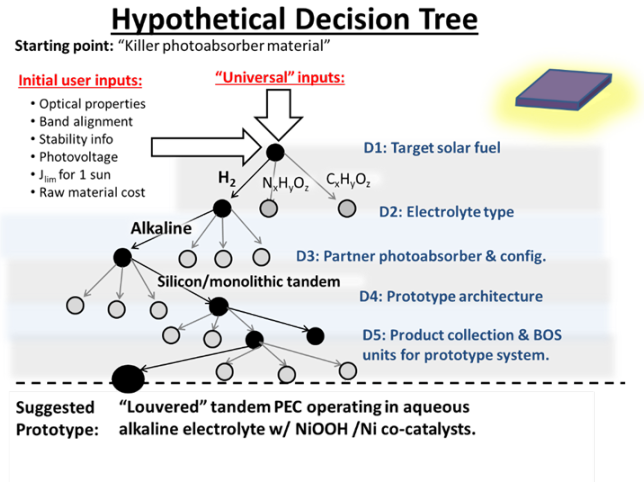

Fig. 3 An example of a Decision Tree for the design of a PEC device for solar fuels production that starts its flow through decision points "D" with a novel photoabsorbing semiconductor and concludes with a prototype design. Details on the use of this Decision Tree are given in **S2**.

with a special role for electrochemistry where ionic path length and electrolyte conductivity within the system can be size limiting.[36-37] PEC devices will require a careful design and optimization of the coupled mass transfer involved in ion transport, product transport and separation, charge generation, transport and separation, and the heat transfer from radiation absorption in order to estimate how a scaled-up version would appear.[38] This complicated and coupled multi-physics nature of functional PEC devices and scale-up activities points to the general need for modeling frameworks and relevant experimentation which can deconvolute the influence of materials, operating conditions, and design on the device performance. An elaboration of these points is provided in **S2**.

From a manufacturing perspective, the starting point for a design idea and subsequent scale-up can be multi-faceted and less strategic or structured. It can be given by economic, sustainability, or safety considerations. It also can be defined by performance maximization, the desire to reduce complexity, the fabrication method in use, which materials are available or desired, availability of prior research scale devices, as well as the nature of the gas and liquid flows downstream.

Different cost minima for different combinations of device components in terms of their performance have been identified by bottom-up techno-economic modeling.[39] In terms of performance, at least two different device design groups can be identified:. One is high-performance, containing expensive component materials with high current density operation, driven by economics, and resulting in highly engineered systems that have large hydrogen production rates. This is solar farming with applications such as production of fuels or chemical commodities. Another has reasonable performance, though optimized, with low cost component materials and a low current density operation in simple systems with low production rates, a form of a "solar leaf."

While undergoing scale-up, the assessment of the device performance will be essential to establish the potential market competitiveness of the approach chosen, and this assessment will rely upon the foundation of an analytical facility for PEC fuel devices. The performance data collected along the scale-up path will give an indication of the size at which smaller prototype measurements can be used to extrapolate efficiency of scaled-up devices and systems.

In consideration of the problem of CO_2 reduction, it should be noted that it need not be a PEC problem, although water splitting to hydrogen and oxygen is. In the photosynthetic membrane, NADPH is used to drive the Calvin cycle for CO_2 reduction in a dark reaction. Although water splitting is thermodynamically uphill, the reaction of carbon dioxide with hydrogen to most useful fuels is thermoneutral or energetically downhill.[40] In view of these energetics, the two device path: H_2O to H_2 and O_2 via PEC and then H_2 + CO_2 in the dark has several merits. First, it avoids the kinetic complication of H_2 formation during CO_2 reduction. The need for a membrane is reduced, as the liquid fuel does not need to be isolated from the anode. Fuels separation is intrinsically easier with the possibly no need for separation as water can be avoided as a medium to perform the CO_2 reduction. The solar fuels community can then make use of organometallic/ catalysis science in the creation of new pathways for CO_2 reduction. Significant changes in the chemical engineering of the prototype design would result from pursuit of this pathway. Within this CO_2 reduction chemistry would also need be the difficult process of CO_2 concentration to increase its low, 400 ppm presence in the atmosphere to a level suitable for practical use.[41-42] It allows the approach to CO_2 concentration to be separated from the PEC ones and to be updated without affecting the initial PEC solar photoconversion technology.

3.

Novel Semiconductors and Coatings

Learning drawn from many years of the development of PV solar cells has brought the awareness that high photon conversion efficiencies and photo-stability are pivotal issues to be considered for PEC devices. This is in addition to the requirement that the PEC semiconductor and other materials be inexpensive or cost-effective since it is a commodity chemical that is being produced in solar fuels evolution. This combination of efficiency and cost is even more important for all processes of solar fuel production compared to PV given the expectation of a significantly higher balance of system costs connected with the design of a PEC cell.[13,15,43]

Here a perspective is given of the required characteristics of the semiconductors to be used in a PEC cell, with supplementary information **S3** containing a more detailed supporting discussion. It will cover the means through which high quality semiconductors can be made more cheaply or novel solids may be discovered, their performance optimized and their suitability for scale-up assessed. The deposition technique and maximum practical size will be seen to be specific to the class of materials under consideration, with the areal dimension being evaluated relative to the 100 cm^2 reference area mentioned previously from present PV solar cell components.

There are a number of inherent physical properties that the central photoactive semiconductor must possess in order to attain efficient solar fuel production, in addition to its area scalability.[8] There must be a suitable exploitation of the solar spectrum in the absorption of light by the semiconductor. This photon absorption must result in sufficient chemical potentials for electrons and holes in the conduction and valence bands where non-radiative recombination in the bulk and at interfaces has been minimized. Charge separation and transport need be effective, which is possible through the control of the carrier mobilities, the appropriate contacts for charge separation, and the requisite velocities of the chemical kinetics of water oxidation. Finally, sufficient stability of the interface must be attained or maintained through control of chemistry, or through chemical passivation or coatings on the semiconductor.

The first two elements of light absorption and chemical potential interact through the energetic, thermodynamic and kinetic conditions for water splitting. Only absorbers with large band gaps can efficiently produce H_2 in a single junction PEC cell. The energy gap needs to be larger than 2 eV considering the 1.23 eV potential for water splitting to be derived from the chemical potentials of electrons and holes in the absorber layers, the entropic loss from those energies involved in the establishment of quasi-fermi levels, and the energy loss involved in the kinetic barriers to fuels evolution.[44] Hence, in a PEC cell, when utilizing single absorber device structures, the maximum solar-to-hydrogen (STH) efficiency appears to be limited to values lower than 15% at one sun AM1.5.[38] Smaller band gap structures are possible if tandem structures are employed in a two junction PEC cell where the tasks of oxidation and reduction steps are driven at different energies of the solar spectrum. As a result, using tandem cells much higher STH efficiencies can be achieved, potentially up to 25%.[30,31]

Examination of past research for semiconductors that satisfy these requirements will reveal many advances, but also a search that is still in progress. Shortcomings in materials properties are to be found in the photo-instability of the solid, its spectral response, and its charge carrier mobility and recombination lifetime. Recently the field has bifurcated into the search for and development of new semiconducting materials that are stable, cheap and efficient and the deposition of thin protection layers onto materials that already produce high efficiency solid state solar cells.

Although some satisfaction can be gained in the latter case by producing devices that split water with 1-10% efficiencies and producing curtains of bubbles for demonstrations, the gain from an immersion of a multilayer solar cell into a solution , as opposed to the advantages of the conformal and spontaneously produced single semiconductor-liquid junction, may be problematic given the required stabilization for the solar cell by a thin protection layer where a small defect or scratch may be fatal and thicker layers are required.[45-46]

Therefore there is a need to discover new defect tolerant semiconductors that are inexpensive, stable in the desired electrolyte, and scalable to a large area and yet can attain a cost-effective efficiency in operation. For a tandem system, two such semiconductors are needed. The focus of the discovery effort here is on solids for an efficient H_2 production system, as opposed to CO_2 reduction systems, given the fallback pathway of conventional catalytic chemistry to take H_2 and CO_2 to other fuels, if need be. For both systems, a key solid is the semiconductor for the requisite oxidation of water as the source of electrons for the reduction reactions.

In the search for new semiconductors for PEC fuels production, two paths present themselves for discussion, combinatorial and computational. Combinatorial approaches have been developed and are now in use for high through-put discovery and optimization of new semiconducting solids.[47] For the most part, present combinatorial approaches to discovery of suitable photoactive semiconductors for PEC have been directed towards metal oxide compounds [45,47-56] Fertile ground is expected in the oxide materials, since they can be very stable and they are known to exhibit unexpected and exceptional properties, such as high T_c superconductivity, multi-ferroic phases, and exotic magnetic phenomena. With this great variability in behavior being evident, the expectation of the discovery of a stable, defect tolerant, low bandgap semiconductor, or class of semiconductors, with appropriate band gaps may well be possible. [27] In addition, improved computational techniques are now able to do a credible job of both predicting band gaps, carrier mobilities, and synthetic approaches.[48] However novel solids may be discovered, their method of synthesis must be translatable to a manufacturing process for them to have a practical impact. More recently the coupling of computational and experimental science has greatly accelerated the rate at which types of materials can be considered and evaluated, as is elaborated in **S3**.[48] This contrasts with more empirical, laboratory-based synthetic quest for new PEC materials and electrolysis materials. While the computational tools to predict new PEC materials have improved dramatically, making the compounds is another manner. To this end recent efforts in computational materials science have begun to address the ability to predict synthetic pathways with some notable successes.[48] Overall, the ability to identify potentially interesting structures and their functionality, when coupled with some insight on how to achieve them synthetically may open a significant new window into the development of new materials for PEC.

Adamantine semiconductors represent an excellent example of how a single class of compounds with group properties may be exploited for use in PEC systems and this is discussed in greater detail in **S3**. The attraction of the adamantine class for a wide range of electro-optical applications is that their electronic structure may be tuned smoothly via the composition of multinary compounds.[57] III–V materials are highly tunable in their bandgaps, band offsets and lattice-constants through the choice of the stoichiometry of multinary compounds. In addition, metal-organic vapor phase epitaxy
(MOVPE) is well-established for III–V compounds at an industrially relevant scale. This type of variability within a single group of compounds presents many options for optimization of PEC performance.

Synthesis	Tooling	Characteristics
Physical	Spin coating (wet)	Substantial waste, limited for multilayers
	evaporation	Low melting materials only
	Magnetron sputtering	Fast, high quality films
Chemical	ALD	Very slow, limited chemistries
	CBD (wet, Chemical Bath)	Slow, poor quality, high waste
	CVD	Faster than ALD, high contaminants
	Reactive spin coating (wet)	Substantial waste, few materials
	Plasma ALD/CVD	Faster, can be high quality
	Spray pyrolysis (wet)	Fast, best for oxides
	Ink jet (wet)	Low waste, best for small (patterned) areas
	Electro/electroless plating (wet)	Best for metals, semiconductors, high waste
	Sol-gel/slurry (wet)	Low waste but poor quality

Fig. 2 Summarized from ref. 58, some common large area deposition technologies are tabulated along with their prominent characteristics.

The large area, material-efficient fabrication of high-performance photoactive thin films has benefited from considerable engineering improvements and now successfully incorporates a great array of wet and dry deposition technologies to create thin film stacks in a continuous, roll-to-roll process on flexible strips or rigid panels.[58] A summary of these methods from ref. 53 is given in Fig. 4 with greater detail given in **S3**. The dry methods involve processes such as thermal and plasma-assisted atomic layer deposition[59-62] sputtering and evaporation[63-65] and the wet methods[66-67] include application of inks and pastes or chemical sprays with subsequent thermal processing. These processes work best for chemically uncomplicated, amorphous materials or composites using nanoparticles. In general, materials systems manufactured in this way have lower photovoltaic performance than that obtained using laboratory scale processes, which is considered to be an acceptable tradeoff for the reduction in process complexity and cost. Process chemistries are often sold with processing tools, however, and it may not be possible to vary reaction conditions enough to fundamentally improve film performance. These various deposition chemistries do present, however, an opportunity to reimagine pathways for materials synthesis so that routes can be found to large area, complex materials and to cost-efficient syntheses of materials optimized at a small scale without loss of performance in their scale-up.[68-71]

4.

Durable Interfaces

Research on durable interfaces for PEC solar fuels production has not yet yielded a photoactive semiconductor interface that is stable in solution and it is a pragmatic approach to present device development to expect that any such discovery is in the future. The immediate goal is then to develop an interface that is stable for a period that exceeds its payback cost and provides a financial benefit in the production of fuels. At present, however, there is no standard for the minimum level of 'tolerable metastability' for a photoelectrode system to render it feasible/practical.

Success in the discovery and development of such an interface will require the control and understanding of failure and of its mechanisms. The pathways for interfacial degradation of a photoactive semiconductor in contact with water are as varied as the number of different semiconductor electrodes that have been studied. However the methodologies for probing

these mechanisms are not always clear, especially, for example, when failure initiates at defects, edges and design junctions in the device.

In the long run it is desirable that the materials composing the interface - the absorber and the catalytic surface – should be earth abundant in nature. In time, command of the catalytic nature of these abundant elements will approach those of present noble catalysts and they will play an essential role. However, it is not yet established how to stabilize even the present expensive catalytic elements in PEC prototypes and it is a pragmatic approach to use them in the development of an introductory application of this technology until such time as their earth abundant counterparts become viable. The use of such expensive catalytic elements will influence the market entry point in Fig. 1b of a business seeking to make a PEC product, but the judicious use of such catalysts should not be a barrier to technology introduction. The century long use of silver by the photographic industry as a catalytic element in a consumer product is a good demonstration that this can be done.

This discussion of durable interfaces illustrates how research towards a more stable catalytic semiconductor electrode has progressed from the simplicity of a conformal junction created through insertion of the photoactive semiconductor into water to structured and designed interfaces designed for catalytic activity and stability. In a consideration of interfacial kinetics and failure mechanisms for semiconductor interfaces, knowledge of semiconductor electrodes under illumination and their method of study are the basis for exploration of means to suppress failure through the acceleration of competing, fuel-producing reactions at the surface. An expanded discussion on this topic is provided in **S4**.The cooperativity of an extensive interaction between semiconductor and surface catalytic structures can also be found to exist, connoting an extensive interaction which extends to systems where self-repair mechanisms are operative. The topic of buried p/n junctions to increase photovoltages is addressed as will also overlayers where unstable light absorbers are covered with very thin stable surface structures to effect the desired fuels production.

The degradation of the semiconductor/electrolyte interface can follow either electrochemical or chemical pathways, or a combination of the two. Although the Gerischer view[72] on the fundamental thermodynamic criteria for electrochemical degradation has shaped thinking on semiconductor photoelectrode corrosion for several decades, this framework does not provide any insight on how *rapidly* a material will decompose. For example, charge-transfer and corrosion/oxidation kinetics can be affected by surface states and electrode self-passivation, where the latter is the formation of an insoluble product layer from the initial semiconductor dissolution/oxidation that can both negatively and positively impact photoelectrode operation. A pragmatic approach to this question of competitive kinetics in solar fuels production has been taken in recent benchmarking measurements of catalysts on semiconductors where screening has been done for both the HER/OER overpotential and the durability.

Advances in this control of kinetic processes will rely upon the most relevant and insightful experimental methods that can and should be employed to understand photoelectrode degradation mechanisms. In recent years, an array of powerful *in situ* and *operando* characterization tools have been developed to offer new routes to overcoming knowledge gaps relating to material transformations in active environments, a summary of which is given in **S4**. However, many of these methods have not been fully utilized to study semiconductor corrosion/oxidation processes. These range from techniques present in the laboratories of most individual researchers to sophisticated measurements for specific photosystems, as might be found in the dedicated analytical facility discussed earlier to beamline end station experimentation at large synchrotron facilities.

The complexity of the energetic and kinetic interaction between semiconductor and surface catalytic structures leads to a cooperativity between them in the overall system behavior. Whereas the thermodynamic concepts of Gerischer [72] serve as a useful guide for design of PEC interfaces for solar fuels when the interface is only slightly perturbed from the model system, at the extrema of pH 0 and 14 in PEC water splitting or when oxide layers are formed or catalytic deposits are made on the surface, significant deviations in behavior can be found and it becomes more effective to assume a more cooperative viewpoint of the components and processes

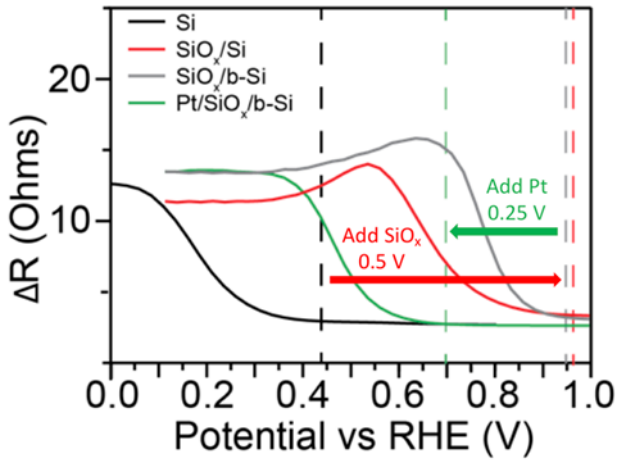

Fig. 3 The thermodynamic flatband potential Ufb measured by intensity-modulated high frequency resistivity (IMHFR) spectroscopy at p-type Si electrodes shifts from the bare, hydrogen-terminated Si surface to more positive potentials as an oxide layer is formed

within the interfacial region. Semiconductor band positions measured in pH 0 electrolyte can vary widely, far greater than beyond the quoted "uncertainty in the band edge positions of a few tenths of an eV for most semiconductors."[73] For example, depending on whether a smooth or stepped surface is exposed, the band positions of WSe_2 can vary by 0.5 V,[74] which can result from the various preparation and handling methods that result in differing surface state densities. In addition, intentional or unintentional interfacial layers can be non-innocent to the energetics, especially when they change the surface isoelectric point (IEP).[75] Thus, the energetics of any semiconductor can be modified by applying an oxide coating with a different IEP as is reported for p-type Si photocathode where U_{fb} can be changed by over 0.5 V simply by growing native oxide on the surface.[76] It can then be shifted by ~-0.25 V through addition of a Pt catalyst to the surface to generate a new electrode with the interfacial structure $Si|SiO_x|Pt|$electrolyte. This is depicted in Fig. 5. This latter result also demonstrates that any interfacial change made to optimize the kinetic overpotential for catalysis will also influence the thermodynamics through U_{FB}.

In such cooperative interfaces, the internal regions of the semiconductor can be controlled with the use of the well-established technology of thin layer electronic devices. From this source come the concepts of buried junctions and overlayer structures to separate light absorption and transport from catalytic fuels production. Various forms of p/n junctions have been used internal to the reactive surface in contact with solution,[26] but their common effect is to reduce electron-hole recombination

and to preserve the hole concentration near the oxygen evolving surface, quantified as a more positive potential for the quasi-Fermi level for holes. Through hole transport, however, this quasi-Fermi level is coupled to the rate of the catalytic oxygen evolving reaction at the surface, implying that if there is a need for a buried junction, the rate of the catalytic reaction is not fast enough – an infinitely fast catalytic reaction, were it possible to react with that velocity, would not require a buried junction. It is certainly a pragmatic approach to PEC fuels evolution technology, however, that until mastery of the catalysis brings about such fast reactivity, cooperative or thin layer junction structures remain a viable and pragmatic option. In the long run, however, the expense of thin layer structures could result in their disappearance from PEC devices in favor of faster and better controlled chemistry for oxygen evolution.

Two classes of thin layer structures and p/n junctions illustrate the options open to PEC devices. In one, charge transport to the catalytic surface is perpendicular to light absorption as in the case of Si microwires grown on a planar surface.[26] This arrangement can compensate for low transport velocities. In the other, the plane of a buried p/n junction PV device is parallel to the reactive surface and charge transport is perpendicular to the junction.

Overlayer structures have a different purpose and are an example of an interface that can integrate solid state structures and surface catalysis in a designed fashion. The interface takes advantage of the electronic coupling of high performance catalysts with high efficiency photovoltaic absorbers while simultaneously protecting the light absorbers from inherent instabilities discussed earlier for the chemical and/or (photo)electrochemical conditions used in either proton/CO_2 reduction or water oxidation. Overlayer coatings also promise additional degrees of freedom to achieve favorable band alignments at an electrode surface while maintaining efficient light absorption and carrier separation using state-of-the-art photovoltaic materials.

Deposited coatings on nominally unstable semiconductor photoelectrodes have a long history, [73] including layers produced by evaporation, chemical vapor deposition and electrodeposition. However, reports on the synthesis of protective metal oxide coatings on silicon photoanodes/ photocathodes using atomic layer deposition (ALD) are more recent.[46,77,78] ALD has a surface-saturating deposition mechanism, which leads to film closure at nanometer thicknesses over complex and rough substrate surfaces[79] and to minimum pinhole formation. As is described in **S4**, the practical aspects of the PEC use of an overlayer have been illustrated through the study[80] of the stability of ALD-TiO_2 coatings, often used to protect silicon photoanodes from corrosion during long-term exposure to water over a range of pH. This includes the evaporation of iridium on the TiO_2 as a catalytic layer for oxygen evolution.[81] Failures of ALD-TiO_2 coated silicon photoanodes are associated with local OER catalyst loss,[82] which is a shift from earlier historical work where research on interfacial stability focused on overlayer delamination from the light absorber. The enhanced ability of techniques such as ALD may shift the main stability concern of researchers from delamination to catalyst adhesion as a failure mechanism.

Summary and Conclusions

There are a range of market sizes and costs for solar fuels production into which a practical PEC device for solar fuels production may be introduced. A flow of discussion was presented in this perspective that begins with this initial market size/cost decision and results in an efficient technical effort in PEC solar fuels research as it defines the sequential constraints of the scope for prototype selection, the device design with its concomitant chemistry and electrochemistry, as well as the semiconductor materials suitable for the photoactive area, and the approach to the creation of a photocatalytic interface with sufficient durability.

Given the number of prototypes being assembled for PEC solar fuels production and the wide range of their design and degree of sophistication, it is evident that an analytical facility is needed to provide a third party verification of their efficiency and performance. The instrumental scope of a PEC facility would be greater than present facilities for determination of PV efficiencies because of the wide span in design in chemical engineering and chemical fuels harvesting in the prototypes. In particular, a large collection of analytical chemistry techniques would be needed in such a facility. Its initial setup will therefore require research in analytical chemical techniques for fuel identification and quantification to complement the carryover of learning from present PV test facilities. In a similar way, a greater array of instrumental analyses for components of a PEC device would be needed, which may preclude an all-encompassing centralized testing center as it may extend to testing at beamline end stations at synchrotron facilities.

There are a great many designs of PEC prototype devices that can be envisioned, but the specific form of an advanced prototype will be determined by the commercial market that it is envisioned to serve. More than one pathway can be taken to compose this prototype design given the many systems and materials explored in the literature and logical decision trees can be constructed to enable final design selection. The prototype must be sufficiently large to capture the potential of the scaled-up version, but would be constrained in size by the size limitations of the analytical facility. Some prototype designs lend themselves to the dimension of a manufacturing scale up. CO_2 reduction can be done inside or outside this device, the latter being a separate technical effort.

Research on novel semiconductors has discovered many candidates for PEC photoabsorbers and photocatalysts and their required properties have been identified. Given the larger area requirements of the prototypes, however, it is evident that the effective approach to discovery of new semiconductors must include the inherent ability of the material to be scaled up in size through any of the many methods that exist for large scale semiconductor material deposition. Several approaches for the discovery of novel semiconductors and the creation of large area deposition are already being established in the present technical community. These include combinatorial and computational approaches which include this scale-up characteristic either inherently or with its inclusion within the combinatorial algorithm. Research with high quality and expensive semiconductors such as the adamantines has illustrated that when a class of compounds is selected or discovered, many possible composition variations and quantum and surface structures are available for use in the design of the interface.

The durability of the interface between these semiconductors and the interface under illumination will dominate the energy and financial payback times of a PEC device. Given the stability limitations of the interfacial compositions explored to date, it is evident that a cost-effective version of a particular prototype and its requisite area will require a coordinated combination of chemistry, electrochemistry, catalysis and the technology of thin layer semiconductor devices. The balance of each of these in the durable interface will depend upon the nature of the semiconductor, the electrolyte, its area and its configuration within the prototype.

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